



Inhibiting effect of decan-1-ol on the transformation of *n*-hexadecane over a Pt/SiO₂–Al₂O₃ catalyst

A.S. Guedes^a, C. Fontaine^a, C. Bouchy^b, S. Brunet^{a,*}

^a UMR CNRS 6503, Catalyse en Chimie Organique, Université de Poitiers, Faculté des Sciences Fondamentales et Appliquées, 40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France
^b IFP Energies nouvelles, Direction Catalyse et Séparation, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

ARTICLE INFO

Article history:

Received 27 May 2010
 Received in revised form 18 July 2010
 Accepted 22 July 2010
 Available online 30 July 2010

Keywords:

Hydrocracking
n-Hexadecane
 Bifunctional catalysts
 Oxygenated compounds
 Platinum
 Silica-alumina

ABSTRACT

The conversion of the *n*-hexadecane, a model molecule representative of LTFT waxes, was studied in the presence of decan-1-ol, a model molecule representative of the most abundant oxygenates present in LTFT syncrude, over a Pt/SiO₂–Al₂O₃ conventional bifunctional catalyst under hydrocracking conditions. A negative and irreversible impact of the presence of alcohol was demonstrated corresponding to a decrease of the activity of the catalyst and a modification of the selectivities towards isomerization and cracking. The real contaminant was water produced by the total transformation of the alcohol. The selectivities towards isomerization and cracking were modified in favour of isomerization in the presence of low amounts of oxygenates. Moreover, characterization of results suggested that the catalyst was irreversibly modified after exposure to alcohol or water, as Pt sintering and diminution of the total acidity of the catalyst.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

In the last years, the production of liquid fuels from various sources (coal, gas and biomass) via the Fischer-Tropsch (FT) process has focused many attentions again. In particular, diesel fuels produced according to this process exhibit outstanding properties compared to diesel fuels derived from crude oil: very high cetane number (typically above 70) and virtually no sulfur, nitrogen or aromatics, resulting in reduced emission of pollutants in the atmosphere [1–6]. However, the highly paraffinic nature of the FT products confers to the diesel fuel unacceptable poor cold-flow properties for commercial purposes.

The commercially followed route in Low-Temperature Fischer-Tropsch (LTFT) synthesis is to produce heavy waxes and then to hydrocrack them to middle distillates (kerosene and diesel). The hydrocracking catalysts for LTFT waxes should therefore meet the following requirements: maximisation of the middle distillates production, improvement of the cold-flow properties of the middle distillates (formation of branched products), limitation of the production of lighter cuts like LPG and naphtha and isomerization of the straight run middle distillates if present in the feed. Hydrocracking and hydroisomerization reactions can be performed over a wide range of catalysts [1,2,5–20], typically bifunctional catalysts with a hydrogenation/dehydrogenation function and an acidic

function. Since the FT products are almost sulfur free, the preferred metal phase is a noble metal, such as Pt and Pd [5,21–23]. Various acidic supports are commonly used in bifunctional catalysis, such as amorphous oxides like silica-alumina or mixture of oxides [7,24–26]. Published work about middle distillates production via LTFT waxes hydrocracking showed that higher yields can be obtained using solid acids with weak or medium acid strength like silica-alumina- or silicated alumina [3]. The acidity of the catalyst has a major influence on the hydroisomerization and hydrocracking yields. The acid site density and acid strength distribution are both important parameters and the proper balance of these variables is critical in order to determine the reactivity and selectivity of the bifunctional catalysts. Hydrocracking of LTFT waxes has been carried out using a diversity of catalysts [1,2,6,20,27–32], similar to those conventionally used for hydrocracking of petroleum-derived feeds. Hydrocracking/hydroisomerization usually follows the classical bifunctional mechanism which can be divided in various elementary steps involving hydro/dehydrogenating (HD/DHD) catalytic sites, and Brønsted acid sites, each type of site playing a particular role [19,33]. In hydrocracking of LTFT wax, the occurrence of hydroisomerization always before hydrocracking is particularly interesting since the formation of some branched cracked products is beneficial for the cold-flow properties of the middle distillates cut. The balance between the number and the activity or strength of the metal and the acid sites plays a role in the products selectivities observed in hydrocracking as well as the operating conditions, including the contaminants that may be present. As well demonstrated by some authors the presence of

* Corresponding author. Tel.: +33 549453627; fax: +33 549453897.

E-mail address: sylvette.brunet@univ-poitiers.fr (S. Brunet).

inhibitors (poisons) in the feeds can significantly affect not only the activity of the catalyst, but also its selectivity if the poison is specific to one of the two functions and affects the balance between the activities of the hydro/dehydrogenation function and the acidic one. In addition the great impact of the balance between acidic and hydrogenating functions during the conversion of *n*-alkanes has also been studied by many authors. It is important to have in mind that in a well balanced catalyst the deactivation is very slow and the *n*-alkane is transformed successively into monobranched isomers, dibranched isomers, and tribranched isomers plus the cracking products [17,34,35], this is a characteristic of an *ideal* bifunctional catalyst.

It is known that syncrude from LTFT contains by-products like oxygenates (mainly alcohol but also carboxylic acid, ketone, etc...). In the absence of any hydrotreatment step, hydrocracking of C₂₂₊ fraction of the feedstock takes place in the presence of these oxygenates [20,36–38]. However studies about the reactivity and impact of these oxygenated compounds on hydrocracking catalysts are scarce and this point can be of crucial importance, as both the activity and selectivity of the catalysts towards liquid fuels can be affected. Fischer-Tropsch feed is different from crude oil because oxygenates adsorb strongly, olefins tend to crack faster on the catalyst, and the high degree of paraffin linearity requires hydroisomerization before cracking [5,39]. For example alcohols react easily to produce olefins and water on silica-alumina [39]; however, the decomposition of carboxylic acids can lead to different products. Pestman et al. [40] investigated the catalytic behaviour of oxides with platinum, since this noble metal remained in the metallic form in presence of oxygen-containing molecules, they have shown that acetic acid can be decomposed into CH₄, CO and H₂O in the presence of hydrogen or into CH₄ and CO₂ using a Pt/SiO₂ catalyst. Thus, some authors have demonstrated in their work that carboxylic acids can interact with noble metals at relatively high temperature. As a consequence, for hydrocracking catalysts, the HD/DHD activity of the noble metal can potentially be impacted by the presence of oxygenates like carboxylic acids. Moreover, it is also well known in refining that selective hydrogenation catalysts are inhibited by CO [40–42].

The interaction of oxygenates with solid acids has been investigated by a few authors, showing that alcohols, acids and oxygenated compounds can interact also with acidic sites [43–48]. As a consequence for hydrocracking catalysts, the acidic function can also potentially be impacted by the presence of oxygenates.

Leckel [20] who studied the effect of tetradecanol and lauric acid on hydrocracking of FT wax over a Pt/W/SiO₂–Al₂O₃ catalyst observed that oxygenates could change the acid–metal balance of the original catalyst by competitive adsorption on the active sites, and each family of oxygenated product would adsorb preferentially in a different function. Alcohols would adsorb preferentially on the acid sites, increasing the metal-to-acid sites ratio while carboxylic acid would decrease this ratio by adsorbing preferentially on the metallic sites.

Works dealing with the influence of oxygenated compounds on the selectivity of hydrocracking catalysts are in short supply, and are rather scarce in terms of the resistance of the catalysts to oxygenated compounds. The aim of this work is to establish and to understand the impact of an oxygenated compound in the hydrocracking of a long chain *n*-alkanes produced in LTFT process over a Pt supported over silicated alumina conventional bifunctional catalyst. The decan-1-ol was chosen as the model molecule representative of the alcohols found in LTFT waxes and *n*-hexadecane as the model molecule representative of the long chain *n*-alkane. The decan-1-ol impact on the hydroconversion of *n*-hexadecane performed over a conventional Pt/silicated alumina hydrocracking catalyst under typical hydrocracking conditions was thus evaluated. Moreover, after each catalytic test, the catalyst acidic and

Table 1
Physical properties of the Pt/SiO₂–Al₂O₃ hydrocracking catalyst.

Catalyst properties	
Pt (wt.%)	0.47
Pt dispersion (%)	85
SiO ₂ /Al ₂ O ₃ (wt.%)	30/70
BET surface area (m ² g ⁻¹)	297

metallic functions were characterized in order to shed light on the impact of the oxygenate on the catalyst.

2. Experimental

2.1. Catalyst

A Pt supported over silicated-alumina catalyst (supplied by IFP Nouvelles energies) was used for the catalytic tests; physical properties are listed in Table 1. The catalyst was crushed and sieved in the range of particles size from 0.250 to 0.315 mm.

2.2. Catalytic test

Catalytic activity measurements were carried out in a fixed-bed reactor at 335 °C under a total pressure of 50 bar, which was typically loaded with 1 g of catalyst. First of all the catalyst was dried *in situ* at 423 °C for 1 h in nitrogen flow (6 N L g_{catalyst} h⁻¹) and then reduced under atmospheric pressure in H₂ flow (6 N L g_{catalyst} h⁻¹) at 450 °C for 2.5 h. The desired reaction conditions were adjusted (335 °C, 50 bar) and then the model feed was injected into the reactor. An H₂/feed molar ratio of ~13 was used and the Weight Hourly Space Velocity (WHSV, ratio between the *n*-C₁₆ mass flow and the catalyst mass) was of 5.56 h⁻¹ (1/WHSV = 0.18 h, residence time). Various model feeds were injected, pure *n*-hexadecane (*n*-C₁₆, from Aldrich, 99% purity), decan-1-ol (98% pure, purchased from Alfa Aesar, 5 wt.% in *n*-heptane) or *n*-hexadecane spiked with various amounts of decan-1-ol (from 0.5 to 2 wt.%). Additional experiments were performed using water instead of decan-1-ol (9.7 wt.% relative to *n*-hexadecane), in this case experiments were carried out using an additional pump for water injection, and 9.7 wt.% (4.4 bar) water was the lowest amount technically possible to reach with the experimental setup.

The various partial pressures depending of the model feed were reported in Table 2.

The experimental procedure to study the impact of the presence and the amount of alcohol, or water, is presented below:

- *Step 1*: Hydroconversion of *n*-C₁₆ (70% of conversion in order to evaluate the isomerization and cracking properties (1/WHSV = 0.18 h));
- *Step 2*: Hydroconversion of *n*-C₁₆ spiked with a given partial pressure of decan-1-ol or water at the same contact time than previous step;
- *Step 3*: Step 1 is re-established to quantify the degree of deactivation of the catalyst.

Each time, another partial pressure of alcohol or water was studied and a freshed catalyst was loaded into the reactor and the catalytic test performed again from step 1 to step 3.

The transformation of decan-1-ol alone has also been studied (5 wt.% diluted in *n*-heptane, under hydrocracking conditions (335 °C, 50 bar, H₂/feed mole ratio of ~13, 1/WHSV ranging from 0.004 to 0.12 h) over the catalyst and also over the support). Under these conditions, the conversion of *n*-heptane is lower than 3 wt.%.

The Pt/Al₂O₃–SiO₂ catalyst was rapidly stable (after 1 h) and no deactivation was observed for a given operating condition.

Table 2

Partial pressures of the different compounds depending of the model feed ($P = 50$ bar, $T = 340^\circ\text{C}$, $\text{H}_2/\text{feed} = 13$).

Feed	P_{H_2} (bar)	$P_{n\text{-C}_{16}}$ (bar)	$P_{\text{H}_2\text{O}}$ (bar)	P_{alcohol} (bar)	$P_{n\text{-C}_7}$ (bar)
$n\text{-C}_{16}$	46.4	3.57	0	0	0
Alcohol	46.4	0	0	0.1 (5 wt.%)	3.5
$n\text{-C}_{16} + \text{alcohol}$	46.4	3.5–3.6	0	0.01–0.10 (0.25–2 wt.%)	0
$n\text{-C}_{16} + \text{H}_2\text{O}$	42.3	3.3	4.4 (9.7 wt.%)	0	0

2.3. Effluent analysis

Under these experimental conditions, a mixture of gas and liquid was present at the outlet of the reactor. The gas phase was analyzed *online* by means of a Varian gas-chromatograph equipped with an automatic sampling valve, a Supelco Petrocol capillary column (DH 50.2, 50 m \times 0.2 mm \times 0.5 μm film) and a flame ionization detector. Owing to the high boiling point of the reactants, online analysis of the reaction products was not convenient. Consequently, the reactor effluents were condensed and liquid samples were periodically collected (every hour) to be analyzed by gas chromatography. The carrier gas was hydrogen and the analytical conditions were adjusted to obtain the accurate separation namely: an *inlet* pressure of 0.8 bar and a temperature of 300°C for the injector and the detector. The temperature program used was as follows: from 45 to 75°C (2°C min^{-1}) and 45 to 220°C (2°C min^{-1}) to analyze the gas and the liquid phase respectively. The quantification of the gas phase formed during the hydrocracking of $n\text{-C}_{16}$ was made by calibration the gas with an external standard (ethane). The response factors for hydrocarbons are around equal to 1 within a range of carbon atoms. The mass balance calculated for each experiment was around 100%.

2.4. Calculations

The results were expressed and analyzed as follows. Decane, transformation product of alcohol, has been subtracted.

The conversion of $n\text{-C}_{16}$ (C), taking into account the gas and the liquid phases, has been calculated:

$$C(\text{wt.}\%) = \frac{\sum A_{\text{isom}} + \sum_{n=1}^{15} A_{C_n}}{\sum_{n=1}^{16} A_{C_n}} \times 100$$

where A_{C_n} is the percent area for all hydrocarbons with n carbon atoms and A_{isom} is the percent area of all products corresponding to the isomerization of n -hexadecane. Hydroisomerization (Y_{isom}) and hydrocracking (Y_{Cr}) yields were calculated according to:

$$Y_{\text{isom}}(\text{wt.}\%) = \frac{\sum A_{\text{iso C}_{16}}}{\sum_{n=1}^{16} A_{C_n}} \times 100 \quad Y_{\text{Cr}}(\text{wt.}\%) = \frac{\sum_{n=1}^{15} A_{C_n}}{\sum_{n=1}^{16} A_{C_n}} \times 100$$

The hydroisomerization (S_{isom}) and hydrocracking selectivities (S_{Cr}) were calculated by the ratio between the corresponding yield and the $n\text{-C}_{16}$ conversion. The presence of secondary cracking was evaluated by the ratio between cracked products and cracked $n\text{-C}_{16}$ as reported below:

$$\frac{\text{cracked products}}{n\text{-C}_{16} \text{ cracked}} = \frac{\sum_{i=1}^{15} \text{mol C}_i}{\text{mol of } n\text{-C}_{16} \text{ cracked}} \times 100$$

The catalyst loss of activity due to the presence of water or alcohol was calculated by the ratio between the catalyst activity (A) during water or alcohol cofeeding (step 2) and the initial activity (A_0) (step 1). The catalyst activity after cofeeding was calculated considering the ratio between the catalyst activity after water or alcohol cofeeding (step 3) and initial catalyst activity (step 1).

The activity was calculated as follows (C : conversion of $n\text{-C}_{16}$):

$$A(\text{g}_{n\text{-C}_{16}} \text{ h}^{-1} \text{ g}_{\text{catalyst}}^{-1}) = \ln \left(\frac{100}{100 - C} \right) \times \text{WHSV}$$

2.5. Catalysts characterization

Brønsted acidity and platinum particles size of various spent catalysts were respectively measured by lutidine (2,6-dimethylpyridine) adsorption followed by FTIR spectroscopy and by Transmission Electron Microscopy (TEM). The amount of the acid sites was obtained from the integration of the adsorption bands at about 1629 plus 1947 cm^{-1} [49,50]. Infrared spectra were recorded with a Nicolet Magna 550 FTIR spectrometer at a resolution of 4 cm^{-1} and collected 128 scans per spectrum. Catalyst samples were pressed into thin wafers (10–20 mg for each sample) under a pressure of 0.5 t cm^{-2} and activated *in situ*, during 15 h at atmospheric pressure under a hydrogen flow ($60 \text{ cm}^3 \text{ min}^{-1}$) at 450°C , and then followed by 1 h of vacuum (10^{-1} Torr) at 400°C . After cooling down the samples until room temperature, they were degassed under a secondary vacuum ($2 \times 10^{-5} \text{ mbar}$) to collect a background spectrum. Lutidine was adsorbed at ambient temperature (2 mbar) and left to equilibrate for 10 min, then the excess of physisorbed lutidine was evacuated (spectrum at room temperature, $t=0'$). IR spectra were recorded every hour during the thermodesorption of lutidine from room temperature to 450°C by steps of 50°C . The concentration of different acid sites was calculated by using the Lambert-Beer law ($C=((A/\varepsilon)(S/M)) \times 1000$), where C is the concentration of acid sites ($\mu\text{mol g}^{-1}$), A the surface of the peak, S the surface of the wafer (2 cm^2), ε the molar extinction coefficient ($1.13 \text{ cm } \mu\text{mol}^{-1}$) and finally m is the mass of the sample [51]. All the spectra were normalized to an equivalent sample mass of 10 mg. The particles size of platinum was measured by Transmission Electron Microscopy (TEM) using a Philips CM 120 microscope (120 kV) equipped with a LaB₆ filament. The mean particle size and size distribution were determined by measuring the diameter of isolated particles using the ImageJ software [52]. The dispersion (D) was calculated using the following equation: $D(\%) = (6/(\rho_{\text{Pt}} \cdot S_{\text{Pt}} \cdot d(\text{m}))) \times 100$ with S_{Pt} the specific surface area ($275 \text{ m}^2 \text{ g}^{-1}$), ρ_{Pt} the density of the platinum ($21.45106 \text{ g m}^{-3}$) and $d(\text{m})$ is the average of particle size.

Various spent catalysts were characterized by elemental analysis (CE Instruments NA2100 Protein) in order to measure the amount of deposited carbon (after washing with CH_2Cl_2).

3. Results

3.1. Catalytic measurements

3.1.1. Hydroconversion of n -hexadecane

The change of the conversion (C) of the n -hexadecane and the selectivity towards isomerization (S_{isom}) and cracking (S_{Cr}) over $\text{Pt/SiO}_2\text{-Al}_2\text{O}_3$ as function of the residence time ($1/\text{WHSV}$) is reported in Fig. 1. An increase of the conversion with the residence time was noticed corresponding to a pseudo first kinetic order regarding the reactant. In the range of residence time studied (corresponding to conversions varying from 20% to

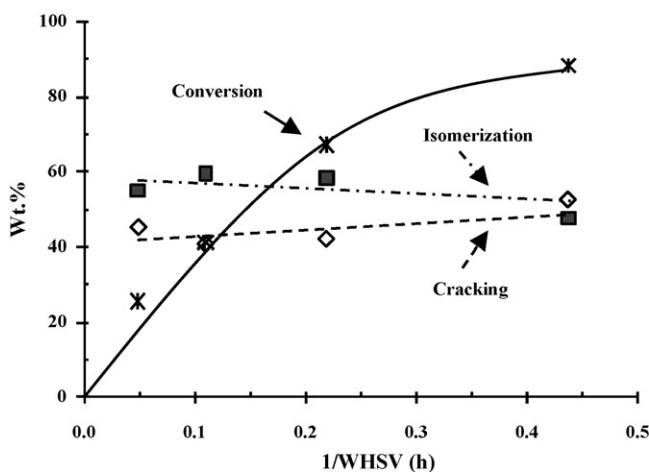


Fig. 1. Conversion of *n*-hexadecane. Conversion and selectivities towards isomerization and cracking, as a function of 1/WHSV (Pt/SiO₂–Al₂O₃, *P*=50 bar, *T*=340 °C, H₂/feed=13 mol/mol).

90%), the selectivities towards isomerization and cracking were rather stable, the isomerization being slightly favoured up to 70% conversion (55%). The monobranched isomers appeared as primary products and their formation increased with the conversion until around 60% and then disappeared for higher conversions (Fig. 2). The yield in cracking products and multibranched isomers increased with conversions. Cracking products could appear as primary products and multibranched products as secondary products.

3.1.2. Conversion of decan-1-ol under hydrocracking conditions

The conversion of decan-1-ol (5 wt.%) diluted in *n*-heptane over Pt/SiO₂–Al₂O₃ catalyst and the support (SiO₂–Al₂O₃) has also been studied under hydrocracking conditions. Under these operating conditions, the conversion of the alcohol was complete whatever the contact time (1/WHSV=0.004–0.123 h). *n*-Decane was the main hydrocarbon product over Pt/SiO₂–Al₂O₃ whereas decenes isomers were the main hydrocarbon products over the support (Fig. 3). Water formation could not be directly quantified with our experimental setup.

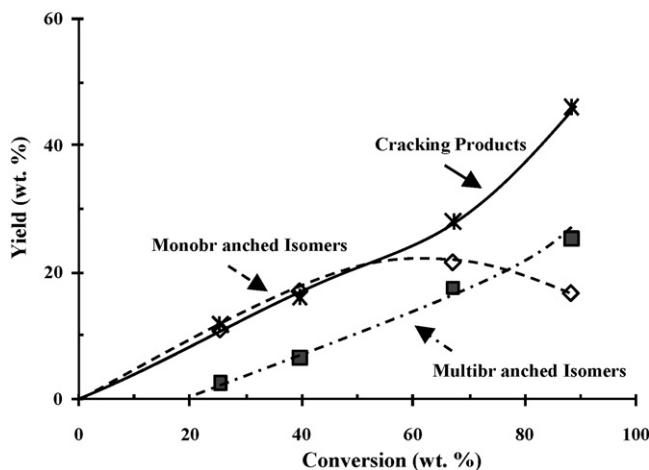


Fig. 2. Conversion of *n*-hexadecane. Yields in monobranched, multibranched isomers and cracking products as function of conversion (Pt/SiO₂–Al₂O₃, *P*=50 bar, *T*=340 °C, 1/WHSV = 0.005–0.50 h, H₂/feed=13 mol/mol).

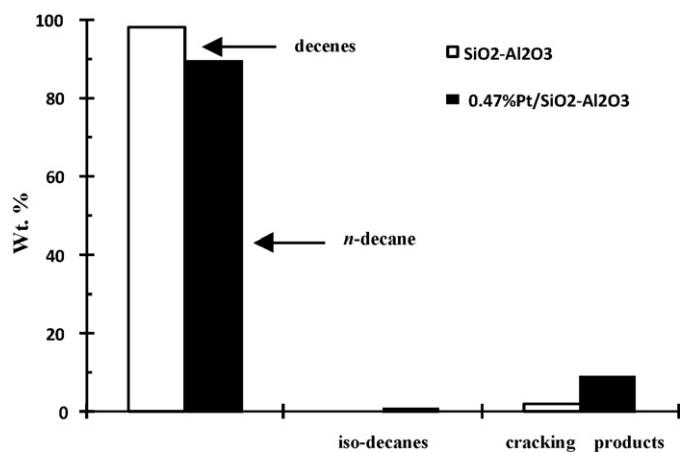


Fig. 3. Transformation of decan-1-ol (5 wt.% in *n*-heptane as solvent) over Pt/SiO₂–Al₂O₃ and SiO₂–Al₂O₃ catalysts. Hydrocarbon products distribution (*P*=50 bar, *T*=340 °C, 1/WHSV = 0.004 h, H₂/feed=13 mol/mol).

3.1.3. Impact of oxygenated compounds on the conversion of *n*-hexadecane

The presence of decan-1-ol in the feed inhibited the conversion of *n*-C₁₆ even when using small amounts. Under these conditions, the conversion of the alcohol is also total whatever the amount added to the feed. A strong decrease of the conversion was observed by the introduction of various partial pressures of alcohol. The catalyst activity decreased from 2.7 to 0.9 g_n-C₁₆ h⁻¹ g⁻¹ when the amount of alcohol increased from 0 to 0.10 bar (Fig. 4a and Table 3). Indeed, a loss of activity measured by the ratio (A/A₀) between the activity (A) for the conversion of *n*-C₁₆ with various amount of alcohol and the activity for the conversion of *n*-C₁₆ alone (A₀), is observed depending of the decan-1-ol amount (Table 3). Thus, a decrease of about 34% was obtained for a partial pressure of 0.01 bar and about 67% for the maximum amount of alcohol (0.1 bar). The presence of the alcohol also induced the modification of isomerization (*S*_{isom}) and cracking (*S*_{cr}) selectivities. The selectivity towards isomerization (*S*_{isom}) (corresponding to the sum of monobranched and multibranched products) increased with the amount of alcohol added to the feed corresponding mainly to an increase of the monobranched products. This corresponds also to a decrease of the cracking selectivity (*S*_{cr}). The comparison of the selectivities, at isoconversion before and with alcohol in the feed indicated that the alcohol cofeeding led to a modification of the selectivities towards isomerization and cracking. Indeed, if we compare, for example, the results obtained in the presence of the highest amount of alcohol (0.1 bar), the conversion of *n*-C₁₆ decreased from 69% to 32% corresponding also to an increase of the isomerization selectivity from 50% to 67% whereas the selectivity towards isomerization does not exceed ca. 55% at 30% conversion when pure *n*-C₁₆ is feeded (Fig. 1). It was also observed that the methane production which is directly related to the platinum hydrogenolysis activity strongly decreased when the alcohol was cofeeded. Indeed, the methane yield (Y_{CH₄}) decreased from 0.13 wt% (no alcohol added) to 0.01 wt% in the presence of 0.01 bar of alcohol. Furthermore, the addition of alcohol led to an irreversible modification of the catalyst, as the catalyst did not recover its initial activity and selectivity when the alcohol was not present in the feed (corresponding to step 3 in the experimental procedure) any more. Indeed, the catalyst activity measured after the treatment in the presence of various partial pressure of alcohol (Fig. 4b and Table 4) was lower than observed before. A decrease of activity from 2.7 to 1.1 g_n-C₁₆ h⁻¹ g⁻¹ corresponding to a loss of activity (A/A₀) of 47–59% after the presence of alcohol in the feed from 0.01 to 0.1 bar was measured. This corresponded also to a modification of the isomerization and cracking

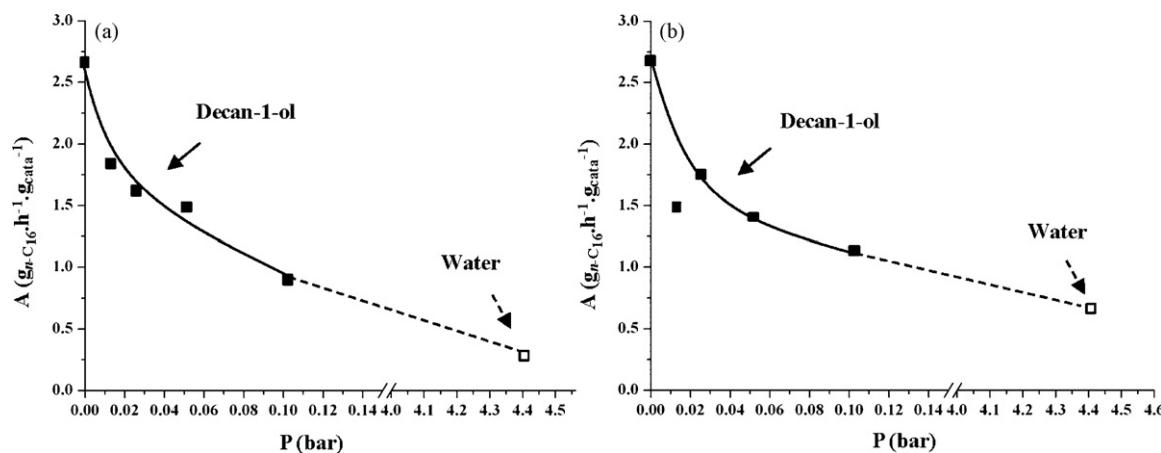


Fig. 4. Catalyst activity. (a) In the presence of various amount of decan-1-ol or water in the feed (step 2) and (b) after the presence of oxygenated compounds in the feed (step 3) ($\text{Pt}/\text{SiO}_2\text{-Al}_2\text{O}_3$, $P=50$ bar, $T=340^\circ\text{C}$, $1/\text{WHSV}=0.18$ h, $\text{H}_2/\text{feed}=13$ mol/mol).

selectivities as the isomerization selectivity increased with the partial pressure of alcohol injected during step 2. When the injection of the alcohol was stopped, even for a small concentration of decan-1-ol present in the feed, the $\text{Pt}/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst appeared to be less active and more selective towards isomerization. In fact, the yield in monobranched isomers was not affected by the presence of the alcohol, contrary to what happens to hydrocracking products and multibranched products (in presence of 0.1 bar of alcohol). The results suggested that the presence of alcohol modified irreversibly the properties of the catalyst. It was also observed that the production of methane disappeared, which confirmed that the hydrogenolysis activity of the catalyst was strongly affected. However, no modification of the distribution of hydrocracking products was observed whatever the amount of alcohol added. Indeed, for example, Fig. 5 reports the distribution of the hydrocracking products obtained without alcohol (step 1 of the experiment), in the

presence of 0.05 bar of alcohol (step 2) and after the treatment with the oxygenated compound (step 3). $\text{Pt}/\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst displayed a symmetrical distribution of hydrocracking products (centered over C_8 hydrocarbons) at the different steps of the experiment, which means for different conversions (from 70% for the step 1 to 45% for steps 2 and 3) and hydrocracking yields (from 34% for step 1 to 14% for step 3) the absence of secondary cracking (cracking products/ $n\text{-C}_{16}$ cracked molar ratio about 2). During step 2 (n -hexadecane spiked with decan-1-ol), an additional formation C_{10} molecules occurred. This behaviour was expected since the decan-1-ol was completely transformed in decane and water, therefore adding extra products with 10 carbon chain length to the hydrocracking products. An additional experiment with water was performed in order to study directly the effect of water. A significant decrease of the conversion was observed (corresponding to a loss of 90%) which was not recovered when the introduction of the

Table 3

Catalytic performances in the presence of various amount of decan-1-ol (step 2). Conversion (C), loss of activity (A/A_0) and selectivities towards isomerization (S_{isom} , S_{mono} and S_{multi}) and cracking (S_{cr}) as a function of the amount of oxygenated compounds (C : n -hexadecane conversion; A : activity of the catalyst for n -hexadecane conversion in the presence of various amount of alcohol, A_0 : initial activity of the catalyst for n -hexadecane conversion in the absence of oxygenate, S_{isom} : selectivity towards isomerization, S_{mono} : selectivity towards monobranched products, S_{multi} : selectivity towards multibranched products, S_{cr} : selectivity towards cracked products and Y_{CH_4} : methane Yield).

	C (wt.%)	A/A_0	S_{isom} (wt.%)	S_{mono} (wt.%)	S_{multi} (wt.%)	S_{cr} (wt.%)	Y_{CH_4} (wt.%)
Decan-1-ol (bar)							
0	69	1	50	29	21	50	0.13
0.01	54	0.66	58	39	19	42	0.08
0.03	50	0.58	69	45	24	31	0.03
0.05	47	0.53	65	44	21	35	0.06
0.10	32	0.33	67	53	14	33	0.01
H_2O (4.4 bar)	11	0.1	54	46	8	46	0.01

($\text{Pt}/\text{SiO}_2\text{-Al}_2\text{O}_3$, $P=50$ bar, $T=340^\circ\text{C}$, $1/\text{WHSV}=0.18$ h, $\text{H}_2/\text{feed}=13$ mol/mol). ($P=50$ bar, $T=340^\circ\text{C}$, $1/\text{WHSV}=0.18$ h, $\text{H}_2/\text{feed}=13$ molar).

Table 4

Catalytic performances after reaction with various amount of oxygenated compounds in the feed (step 3). Conversion (C), loss of activity (A/A_0) and selectivities towards isomerization (S_{isom} , S_{mono} and S_{multi}) and cracking (S_{cr}) (A : activity of n -hexadecane in the presence of various amount of alcohol, A_0 : initial activity of n -hexadecane alone, S_{isom} : selectivity towards isomerization, S_{mono} : selectivity towards monobranched products, S_{multi} : selectivity towards multibranched products, S_{cr} : selectivity towards cracked products and Y_{CH_4} : methane yield).

	C (wt.%)	A/A_0	S_{isom} (wt.%)	S_{mono} (wt.%)	S_{multi} (wt.%)	S_{cr} (wt.%)	Y_{CH_4} (wt.%)
Decan-1-ol (bar)							
0	69	1	50	29	21	50	0.13
0.01	47	0.53	68	45	23	32	0
0.03	53	0.62	74	47	27	26	0
0.05	45	0.50	70	49	21	30	0
0.10	38	0.41	77	56	21	23	0
H_2O (4.4 bar)	25	0.24	81	66	15	19	0

($\text{Pt}/\text{SiO}_2\text{-Al}_2\text{O}_3$, $P=50$ bar, $T=340^\circ\text{C}$, $1/\text{WHSV}=0.20$ h, $\text{H}_2/\text{feed}=13$ mol/mol).

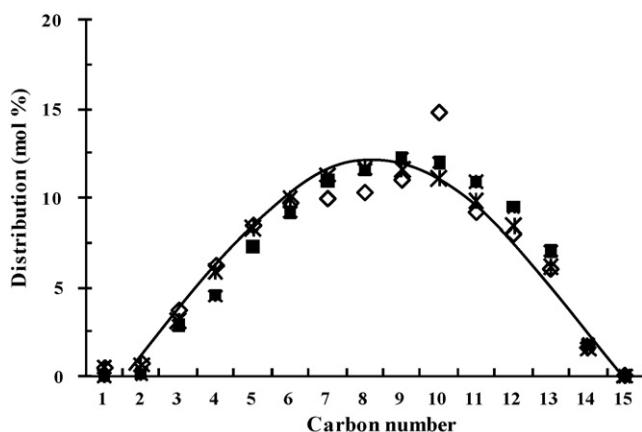


Fig. 5. Molar distribution of hydrocracked products at different conversions (C) of *n*-hexadecane and different hydrocracking yield (Y_{Cr}) before (step 1), during (step 2) and after (step 3) the presence of decan-1-ol (0.05 bar) in feed ($Pt/SiO_2-Al_2O_3$, $P = 50$ bar, $T = 340$ °C, $1/WHSV = 0.20$ h, $H_2/\text{feed} = 13$ mol/mol). (X) Step 1, $C = 70\%$, $Y_{Cr} = 34\%$; (◊) step 2, $C = 45\%$, $Y_{Cr} = 16\%$; (■) step 3, $C = 45\%$, $Y_{Cr} = 14\%$.

water was stopped (Fig. 4a and b). Selectivities did not vary significantly suggesting that a strong alteration of both functions (acidity and hydro-dehydrogenation) might have occurred. The formation of methane also significantly decreased in the presence of water and completely disappeared after the establishment of the initial conditions (Table 4).

3.2. Characterization various spent catalysts

The Brønsted acid properties of the catalyst, the average platinum particle size after the reduction step and after the catalytic tests (conversion of *n*-hexadecane with or without alcohol or water) were characterized by IR spectroscopy of lutidine and by transmission electron microscopy. It can be noticed that the amount of lutidine adsorbed by the spent catalysts decreased when the partial pressure of the oxygenated compound used during the corresponding catalytic test increased. This suggests that the total acidity of the catalyst was altered by the presence of oxygenates in the feed (Table 5). However, the strength distribution of the Brønsted acidity of the sites was not significantly modified (Fig. 6). Indeed, the lutidine desorption was mainly obtained at lower temperature after the conversion of *n*-hexadecane whatever

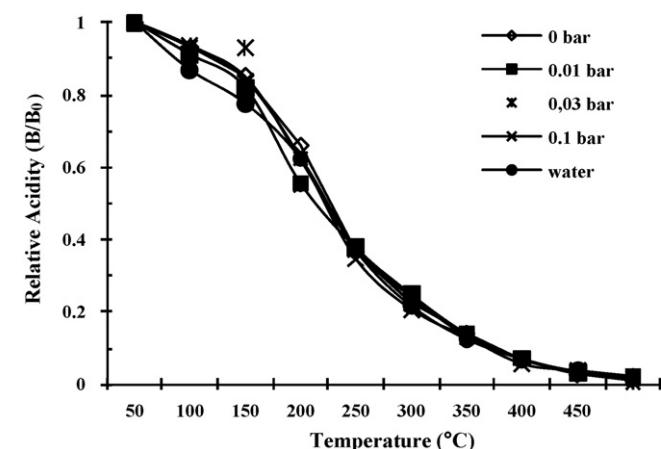
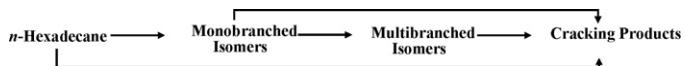


Fig. 6. Relative acidity measured by the B/B_0 ratio (B_0 : total Brønsted acidity measured by Lutidine adsorption at room temperature; B : Brønsted acidity at a temperature) as function of temperature for the $Pt/SiO_2-Al_2O_3$ catalyst after the conversion of *n*-hexadecane in the presence of various amount of alcohol (from 0 to 0.1 bar) or water (4.4 bar).



Scheme 1. Conversion of *n*-hexadecane over $Pt/SiO_2-Al_2O_3$ catalyst ($P = 50$ bar, $T = 340$ °C, $1/WHSV = 0-0.50$ h, $H_2/\text{feed} = 13$).

the amount of alcohol present in the feed or water.

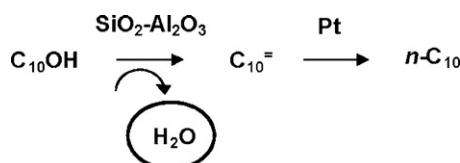
According to TEM investigations, the particle size of Pt was also affected by the presence of the alcohol or water. Indeed, the average particle size increased from 1.2 nm without alcohol to 1.7 nm in presence of 0.10 bar of alcohol and 1.8 nm with water (4.4 bar). This corresponds to a decrease of the dispersion (D) from 85% to 60% with 0.10 bar of alcohol and 54% with water. The results obtained suggested a sintering of the Pt particles in the presence of oxygenates (Table 5). Only minor carbon deposition (~0.4 wt.%) was observed whatever the amount of alcohol added. In the presence of water however 1.5 wt.% of carbon was analyzed on spent catalyst.

4. Discussion

The conversion of the *n*-hexadecane, a model molecule representative of long chain paraffins present in LTFT waxes, was studied over a bifunctional $Pt/SiO_2-Al_2O_3$ catalyst under typical FT waxes hydrocracking conditions. According to Fig. 2, the monobranched isomers appear as primary products, multibranched as secondary products and cracked products can appear as primary or consecutive to isomerization (Scheme 1). This behaviour is not typical of an *ideal* hydrocracking catalyst [22,35,53], where the *n*-alkane is transformed successively into monobranched isomers, dibranched isomers, and tribranched isomers plus the cracking products, which means (de)-hydrogenation reactions occurred much faster than the acid catalyzed isomerization and cracking reactions. This non-*ideal* behaviour may be due to an improper balance of the bifunctional catalyst with the model molecule chosen and the selected operating conditions. Indeed, as reported by Thybaut et al., both the carbon number of the feedstock and the operating conditions (pressure, temperature, molar hydrogen-to-hydrocarbon ratio) can impact the “ideality” of a given catalyst [35,54]. As underlined by Martens et al. [55] for a given bifunctional catalyst and chain length of a *n*-paraffin to be converted there is an optimum platinum loading necessary to obtain an ideal bifunctional catalyst. If the amount of platinum is too small, then some overcracking of the carbocation intermediates may occur on the acidic phase; on the contrary if the amount of platinum is too high, then some hydrogenolysis can be superimposed on the classical bifunctional reaction pathway, and the obtained catalyst is not ideal either. Indeed, they assumed a modification of the partial pressure of olefins formed by dehydrogenation on the noble metal and/or from an enhanced reactivity of these olefins over the acid sites of the catalyst when their chain length increased. During this work, we observed a significant methane production with the $Pt/SiO_2-Al_2O_3$ catalyst (see first line, Table 3). This suggests that with *n*-hexadecane and under

Table 5
MET and IR (lutidine adsorption at 50 °C) characterization of the catalyst after the conversion of *n*-hexadecane with various amount of alcohol or water in the feed (D : platinum dispersion, d_p : average Pt particle diameter).

	d_p (nm)	D (%)	Lutidine ($\mu\text{mol g}^{-1}$)
Decan-1-ol (bar)			
0	1.2	85	197
0.01	1.3	78	195
0.03	1.4	73	182
0.05	1.6	64	–
0.10	1.7	60	155
H_2O (4.4 bar)	1.8	54	145



Scheme 2. Conversion of decan-1-ol over Pt/SiO₂–Al₂O₃ or SiO₂–Al₂O₃ catalysts ($P=50$ bar, $T=340$ °C, 1/WHSV = 0.004 h, H₂/feed = 13).

the selected operating conditions the amount of platinum is too high to obtain an ideal catalyst.

According to the results obtained with the decan-1-ol/heptane feedstock, under the selected hydrocracking conditions, and in accordance with previous work [56], decan-1-ol was totally transformed into decane or decenes over the reference catalyst or the support (Fig. 3). It is proposed that the alcohol is dehydrated into decenes and water over the silicated alumina and that decenes are hydrogenated to produce decane over the platinum particles if present (Scheme 2). The decan-1-ol decomposition appears also to be very fast. Indeed, under the selected conditions, corresponding to an alcohol contact time of 0.08 h, the decan-1-ol conversion is total. For the *n*-hexadecane/decan-1-ol experiments, neglecting the potential *n*-hexadecane competitive adsorption with decan-1-ol at the surface of the catalyst, the amount of catalyst required to totally convert the alcohol can be evaluated. In the worst case scenario (corresponding to the experiment performed with the highest amount of decan-1-ol introduced, i.e. 2 wt.%, i.e. 0.111 g decan-1-ol, see Table 2) the amount of catalyst (m_{catalyst}) required to totally convert the alcohol was calculated considering the contact time for total conversion (0.08 h) and the flow of alcohol (0.111 g/h) during the experiment: $m_{\text{catalyst}} = 0.08 \times 0.111 = 0.0088$ g. ca. 9 mg of catalyst should be necessary to fully convert the alcohol into water and decane/decenes; it represents less than 1% of the catalyst mass (1 g) used under operating conditions for the conversion of *n*-hexadecane.

The presence of decan-1-ol inhibited strongly the conversion of *n*-C₁₆. Activity and selectivity were both affected. A significant loss of activity was observed when adding small amounts of alcohol and then the activity loss was lower. This corresponds also to a change of selectivities. Indeed, the isomerization was favoured and the cracking decreased when the amount of alcohol in the feed increased. In the same time the formation of methane which is representative of the hydrogenolysis properties of platinum also decreased. This means that there is a modification of the balance between the hydro/dehydrogenation (metallic site) and acidic functions (provided by the support). Indeed, in accordance with the literature [39], the alcohol seems to adsorb preferentially on the acidic sites, being totally decomposed in decane and water. Thus the results strongly suggest the presence of a competitive adsorption between the alcohol or more probably water and alkenes at the surface of the catalyst. In the same way, Leckel [20] studied the effect of tetradecanol on hydrocracking of hydrogenated FT wax and also found a decrease of the activity and a modification of the selectivity. The presence of the alcohol improved the hydrocracking selectivity towards diesel. Indeed, it was proposed that the presence of the alcohol modifies the balance of metal-to-acid sites of the catalyst

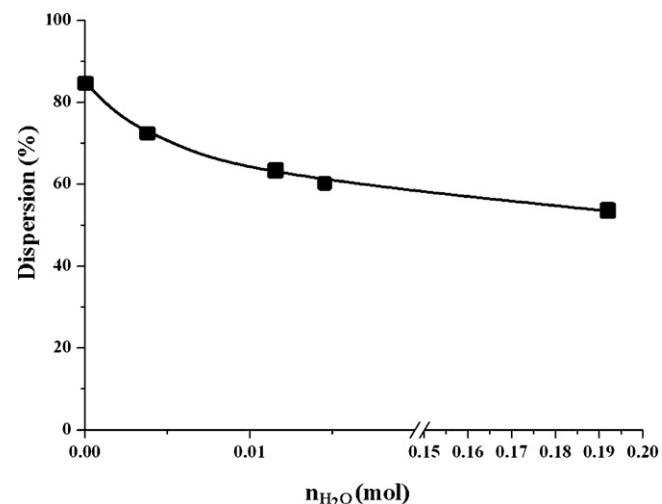


Fig. 7. Dispersion of the platinum particles at catalyst surface in function of the total quantity of water injected or produced via decan-1-ol during the catalytic test.

by a competitive adsorption on the active sites between the alcohol (more polar than the alkenes produced) and the Fischer-Tropsch wax. They considered that there was no modification of the number of the metal sites accessible whereas the number of the acid sites available decreased by competitive adsorption between oxygens and hydrocarbons. In the present work, the decrease of the activity clearly shows the occurrence of at least partial inhibition of the Brønsted acid sites of the silicated alumina but in the same way the strong decrease of the methane yields with the increasing pressures of alcohol in the feed also indicates at least an inhibition of the platinum hydrogenolysis activity.

Moreover, the impact of the decan-1-ol, and mainly water, was found to be irreversible because it was not possible to re-establish the initial properties of the catalyst. The catalyst initial activity and selectivities could not be restored even after a reactivation under hydrogen for 2 h at 450 °C (result not shown here). This confirms that water produced by the dehydration of alcohol may poison or modify irreversibly the catalyst properties (number of acidic sites and sintering of the platinum particles), a decrease of the dispersion with the increase of the total amount of water (mol) injected during the experiments can be noticed (Fig. 7), which is in line with the fact that no more methane formation was observed at the injection of alcohol. Certainly, the sintering of the platinum corresponding to the increase of the particle size and the decrease of the dispersion of the metal could be correlated with the decrease of the formation of methane when the amount of alcohol in the feed raised. These trends would be due to the presence of water as the results obtained when water was directly injected seemed to be in accordance with those obtained with the alcohol. But in the meantime it was difficult (from the experimental point of view) to use concentrations in water in the same range than the amount issued from the dehydration of decan-1-ol, so the impact was much stronger.

According to lutidine characterization, the global acidity of the silicated alumina is also affected by the presence of alcohol or

Table 6

Conversion of *n*-hexadecane over 0.47 wt.% Pt/silicated alumina and 0.05 wt.% Pt/silicated alumina catalysts. Activity, Conversion (C), and selectivities towards isomerization (S_{isom}), cracking (S_{Cr}) and the methane yield (Y_{CH_4}).

Pt (wt.%)	$A A$ (mg _{<i>n</i>-C₁₆} h ⁻¹ g _{cata})	C (wt.%)	S_{isom} (wt.%)	S_{Cr} (wt.%)	Y_{CH_4} (wt.%)
0.47 (without alcohol)	2.8	71	55	45	0.14
0.47 (after alcohol)	1.1	38	77	23	0
0.05 (without alcohol)	1.7	51	96	4	0

($P=50$ bar, $T=340$ °C, 1/WHSV = 0.20 h, H₂/feed = 13 mol/mol).

water (Table 5) in accordance with the global loss in activity, however the relative acid strength distribution of the catalyst remains unchanged (Fig. 6).

Characterization of the catalysts after the injection of alcohol or water has confirmed that the acidity of the catalyst, the average size of platinum particles and the dispersion of platinum were modified by the presence of the alcohol or water. As both the acidic and the metallic functions were affected by the presence of alcohol or water, it is difficult to unambiguously explain the catalyst loss of activity and gain of selectivity. However in light of the results obtained with the fresh catalyst using pure hexadecane, we suggest that the platinum sintering plays a beneficial role when the catalyst isomerization selectivity is considered as sintering deeply suppresses the hydrogenolysis activity of the platinum. In order to check the validity of this hypothesis, a catalyst containing only 0.05 wt.% of platinum deposited on the same silicated alumina support was prepared and tested for the hydroconversion of pure *n*-hexadecane (Table 6). Indeed, this catalyst exhibited a very high selectivity towards isomerisation in unfraction after the lack of absence of methane production.

5. Conclusion

It was found in this work that the activity of a conventional Pt/silicated alumina catalyst for the *n*-wax strongly affected by the presence of deca-1-ol in the feed. The real contaminant was suggested to be water, produced by the total transformation of the alcohol. The activity and the selectivity towards isomerization and cracking were modified in favour of isomerization in the presence of low amounts of the alcohol. Moreover it appeared that the hydrocracking catalyst was irreversibly modified by the alcohol or water as its initial activity and selectivity could not be recovered even when the alcohol or water injection was stopped. According to characterization results, the acidic and metallic functions of the catalyst were both altered as a decrease of the acidity and a sintering of the platinum were observed.

The investigation of the impact of other oxygenated compounds will be carried out in order to globalize the study to other oxygenated compounds present in the LTFT wax, like carboxylic acids.

Acknowledgements

Ana Sofia Guedes thanks IFP and ANRT for a PhD grant. The authors would like also to thank J. D. Comparot for FTIR-Lutidine measurements and S. Pronier for TEM analysis (LACCO).

References

- [1] M.E. Dry, *Catal. Rev. Sci. Eng.* 23 (1981) 265–278.
- [2] D. Leckel, *Energy Fuels* 23 (2009) 32–37.
- [3] C. Bouchy, G. Hastoy, E. Guillon, J.A. Martens, *Oil Gas Sci. Technol.-Rev. IFP* 64 (2009) 91–112.
- [4] A. Martinez, G. Prieto, M.A. Arribas, P. Concépcion, *Appl. Catal. A* 309 (2006) 224–236.
- [5] D. Leckel, *Energy Fuels* 19 (2005) 1795–1803.
- [6] D. Leckel, *Energy Fuels* 21 (2007) 1425–1431.
- [7] F. Chevalier, M. Guisnet, R. Maurel, in: G.C. Bond, P.B. wells, F. Tompkins (Eds.), *Proceedings of the 6th International Conference on Catalysis*, The Chemical Society, London, 1997, p. 478.
- [8] F. Ribeiro, C. Marcilly, M. Guisnet, *J. Catal.* 78 (1982) 267–280.
- [9] J.A. Martens, P.A. Jacobs, J. Weitkamp, *Appl. Catal.* 20 (1986) 283–303.
- [10] J.A. Martens, P.A. Jacobs, J. Weitkamp, *Catal. Today* 1 (1978) 435–453.
- [11] J.A. Weitkamp, P.A. Jacobs, J.A. Martens, *Appl. Catal.* 8 (1983) 123–141.
- [12] C.H. Christensen, I. Schmidt, C.H. Christensen, *Catal. Commun.* 5 (2004) 543–546.
- [13] F.R. Ribeiro, M. Guisnet, in: *Zeólitos um nano mundo ao serviço da cátalise*, Fundação Calouste Gulbenkian, 2004.
- [14] F. Alvarez, F.R. Ribeiro, G. Giannetto, F. Chavalier, G. Perot, M. Guisnet, *Stud. Surf. Sci. Catal.* 49 (1989) 1339–1348.
- [15] M. Guisnet, F. Alvarez, G. Giannetto, G. Perot, *Catal. Today* 1 (1987) 415–433.
- [16] F. Alvarez, F.R. Ribeiro, G. Perot, C. Thomazeau, M. Guisnet, *J. Catal.* 162 (1996) 179–189.
- [17] H.F. Schulz, J.H. Weitkamp, *Ind. Eng. Chem. Proc. Res. Dev.* 11 (1972) 46–53.
- [18] I. Rossetti, C. Gambaro, V. Calemma, *Chem. Eng. J.* (2009) 295–301.
- [19] H.L. Coonradt, W.E. Garwood, *Ind. Eng. Chem. Proc. Des. Dev.* 3 (1964) 38–45.
- [20] D. Leckel, *Energy Fuels* 21 (2006) 662–667.
- [21] A. Corma, A. Martínez, S. Perguer, S. Peratello, C. Perego, G. Bellussi, *Appl. Catal. A* 152 (1997) 107.
- [22] V. Calemma, S. Peratello, C. Perego, *Appl. Catal. A* 190 (2000) 207–218.
- [23] V. Calemma, S. Peratello, S. Pavoni, G. Clerici, C. Perego, *Stud. Surf. Sci. Catal.* 136 (2001) 307–312.
- [24] A. Corma, *J. Catal.* 216 (2003) 298–312.
- [25] K. Fang, W. Wei, J. Ren, Y. Sun, *Catal. Lett.* 93 (3/4) (2004) 235.
- [26] S.P. Elangovan, C. Bischof, M. Hartmann, *Catal. Lett.* 80 (1/2) (2002) 35–40.
- [27] R. de Haan, G. Joost, E. Mokoena, C.P. Nicolaides, *Appl. Catal. A* 327 (2007) 247–254.
- [28] D. Leckel, M. Liwanga-Ehumbu, *Energy Fuels* 20 (2006) 2330–2336.
- [29] D. Leckel, *Ind. Eng. Chem. Res.* 46 (2007) 3505–3512.
- [30] K.M. Cho, S. Park, J.G. Seo, M.H. Youn, S.H. Baeck, K.W. Jun, J.S. Chung, I.K. Song, *Appl. Catal. B* 83 (2008) 195–201.
- [31] Z. Zhou, Y. Zhang, J.W. Tierney, I. Wender, *Fuel Process. Technol.* 83 (2003) 67–80.
- [32] V. Calemma, S. Correra, P. Perego, P. Pollesel, L. Pellegrini, *Catal. Today* 106 (2005) 282–287.
- [33] P.B. Weisz, *Adv. Catal.* 13 (1962) 137–190.
- [34] G. Kinger, H. Vinek, *Appl. Catal. A* 218 (2001) 139–149.
- [35] J.W. Thybaut, C.S.L. Narasimhan, J.F. Denayer, G.V. Baron, P.A. Jacobs, J.A. Martens, G.B. Marin, *Ind. Eng. Chem. Res.* 44 (2005) 5159–5169.
- [36] M. Clays, E. Van Steen, *Stud. Surf. Sci. Catal.* 152 (2004) (Chapter 8).
- [37] G.W. Huber, S. Iborra, A. Corma, *Chem. Rev.* 106 (2006) 4044–4098.
- [38] A. Klerk, *Catal. Today* 130 (2008) 439–445.
- [39] P. Berteau, B. Delmon, J.L. Dallons, A. van Gysel, *Appl. Catal. A* 70 (1991) 307–323.
- [40] R. Pestman, R.M. Koster, J.A.Z. Pieterse, V. Ponec, *J. Catal.* 168 (1997) 255–264.
- [41] P. Mäki-Arvela, I. Kubickova, M. Snåre, K. Eränen, D.Y. Murzin, *Energy Fuels* 21 (2007) 30–41.
- [42] M. Snåre, I. Kubickova, P. Mäki-Arvela, K. Eränen, D.Y. Murzin, *Ind. Eng. Chem. Res.* 45 (2006) 5708–5715.
- [43] M. Cowley, *Energy Fuels* 20 (2006) 1771–1776.
- [44] D. Smook, A. De Klerk, *Ind. Eng. Chem. Res.* 45 (2006) 467–471.
- [45] A. De Klerk, *Energy Fuels* 21 (2007) 625–632.
- [46] I. Rodriguez, M.J. Climent, S. Iborra, V. Fornés, A. Corma, *J. Catal.* 192 (2000) 441–447.
- [47] A. Corma, O. Marie, F.J. Ortega, *J. Catal.* 222 (2004) 338–347.
- [48] M. Demorest, D. Mooberry, J.D. Danforth, *Ind. Eng. Chem.* 43 (1951) 2569–2575.
- [49] A. Corma, C. Rodellas, V. Fornest, *J. Catal.* 88 (1984) 374–381.
- [50] T. Onfroy, G. Clet, M. Houalla, *Micropor. Mesopor. Mater.* 82 (2005) 99–104.
- [51] M. Guisnet, P. Ayrault, J. Datka, *Micropor. Mesopor. Mater.* 20 (1998) 183–291.
- [52] W.S. Rasband, ImageJ, US National Institutes of Health, Bethesda, MD, USA, <http://rsbweb.nih.gov/ij/>.
- [53] M.J. Girgis, Y.P. Tsao, *Ind. Eng. Chem. Res.* 35 (1996) 386–396.
- [54] K. Chaudhari, T.K. Das, A.J. Chandwadkar, S. Sivasanker, *J. Catal.* 186 (1999) 81–90.
- [55] J.A. Martens, M. Tiele, A.A. Jacobs, in: H.G. Karge, J. Weitkamp (Eds.), *Zeolites as Catalysts, Sorbents and Detergents Builders*, Elsevier, Amsterdam, 1989, pp. 49–60.
- [56] E. Licht, Y. Shashter, H. Pines, *J. Catal.* 38 (1975) 423–429.